Thermal decomposition of bis (2-chloroethyl) sulphide and bis (2-chloroethyl) ether between 300 and 500°C

F. Battin-Leclerc [a,*], F. Baronnet [a], G. Paternotte [b],
J.P. Leclerc [b], R. Gourhan [c]

[a] *Departement de Chemie-Physique des Reactions, ENSIC-CNRS, Universite de Nancy,
1 rue Grandville, BP 451, 54001 Nancy Cedex, France*
[b] *PROGEPI, 1, rue Grandville, BP 451, 54001 Nancy Cedex, France*
[c] *51000 Cherbourg, France*

Abstract

The gas-phase pyrolysis of bis (2-chloroethyl) sulphide (usually named yperite) has been investigated in a static reactor in the following conditions, temperatures ranging from 300 to 500°C, an initial pressure of 16.67 kPa with a dilution in nitrogen and reaction times ranging from 1 to 10 min. To obtain a better understanding of the mechanism of the thermal decomposition of bis (2-chloroethyl) sulphide, we have also studied the pyrolysis of the oxygenated equivalent compound, bis (2-chloroethyl) ether, under the same conditions. A 99% conversion of bis (2-chloroethyl) sulphide was obtained at 500°C; the major products detected were vinyl chloride and ethylene. In the case of bis (2-chloroethyl) ether, the major products observed were vinyl chloride, methyl chloride, methane, ethylene and carbon monoxide. For both compounds studied, a kinetic mechanism has been proposed which involves a molecular four-centre elimination reaction and free-radical reactions. The study clearly shows the possible industrial use of this process to destroy agents in chemical weapons and a first range of temperatures and reaction times has been selected for a future reactor design. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Yperite; Bis (2-chloroethyl) sulphide; Bis (2-chloroethyl) ether; Thermal decomposition; Chemical weapons; Pyrolysis

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* Corresponding author. Tel.: + 33-3-83175125; fax: + 33-3-83378120.
E-mail address: frederique.battin-leclerc@dcpr.ensic.u-nancy.fr (F. Battin-Leclerc)

1. Introduction

Low pressure pyrolysis has been proved at the laboratory scale to be an efficient technique to destroy phosgene, diphosgene and chloropicrine [1] gases which are contained in artillery projectiles used during the First World War. Due to the absence of oxygen, the low pressure pyrolysis technique should lead to a much smaller formation of dioxins than the usual incineration units [2]. But to be sure that an industrial process based on this technique could be a possible solution to destroy the agents included in chemical weapons, it is necessary to prove that yperite (bis (2-chloroethyl) sulphide) can also be destroyed by this method. Yperite or mustard gas has been extensively used in chemical weapons and is frequently present in unexploded ammunitions, which are still have found in western Europe near the front line of the First World War.

The only use of bis (2-chloroethyl) sulphide has been in chemical weapons and its production and handling has been extremely restricted (ban on chemical warfare). There is then no published study on the thermal decomposition of this compound in the literature. The gas-phase pyrolysis and oxidation of some ethers have been extensively studied because of their use as anti-knock additives in spark-ignited engines (methyl-*tert* butyl ether [3–6], ethyl-*tert* butyl ether [7]) or as a component of diesel fuels (dimethyl ether [8]); but as far as we know most studies on ethyl ether pyrolysis are not very recent [9,10] and we are unaware of any earlier experimental studies of the gas-phase decomposition of bis (2-chloroethyl) ether.

2. Experimental method

Reactants and nitrogen were introduced in an evacuated spherical reaction vessel made of Pyrex glass (volume 350 ml), which was heated by means of 'Thermocoax' insulated resistors with an Inconel sheeting directly coiled on the glass wall. Fig. 1 presents a scheme of this vessel.

To avoid any problem of condensation, all parts of the apparatus which could not be covered by 'Thermocoax' were heated by a heating cord ($T_{max} = 400°C$). Nevertheless a few cold zones could not be avoided (near the taps or the pressure transducer). A thermocouple was located between the reactor wall and the wires to measure and regulate the temperature. A pressure transducer (0–760 Torr) was directly connected to the reaction vessel. Liquid reactants were introduced from a syringe via a septum in the vessel containing already 13.3 kPa of nitrogen. In the case of a liquid compound with a low boiling point, the presence of nitrogen is necessary to ensure its complete vaporisation. The progress of the reaction was followed by pressure measurements. The pressure profiles demonstrate that no problem of vaporisation occurs, that the reaction is complete and they also show if secondary reactions can happen.

Analyses of bis (2-chloroethyl) sulphide and bis (2-chloroethyl) ether were performed by GC–MS. The mass spectrometer, a Finnigan Mat Ion Trap Detector,

was coupled to a gas chromatograph, which was fitted with a silica capillary column with a CP sil 8 (5% phenyl, 95% methylpolysiloxane) liquid phase, purchased from Chrompack. The oven temperature was maintained at 140°C. The samples for analysis by GC–MS were taken with a gas syringe through the septum which was designed for the introduction of liquids. It was not possible to get samples by freezing the gas leaving the reactor at the end of the set reaction time in a trap maintained at liquid air temperature (as we did in a previous study [1]), because bis (2-chloroethyl) sulphide, bis (2-chloroethyl) ether and some heavy products formed condensed at the outlet of the reactor. It was then not possible to use the internal standard method to analyse quantitatively these compounds.

Analysis of carbon monoxide was performed by conventional gas chromatography with catharometer detection by using a Carbosphere packed column (Chrompack) maintained at 40°C. Light organic compounds were analysed by conventional gas chromatography with flame ionisation detection by using a Squalane packed column at 80°C isotherm and a Carbosphere packed column (Chrompack) at 150°C. Gas phase samples were directly obtained by expanding the gas from the reaction vessel. Quantitative analyses were obtained by using calibration curves of pure gases. Injections were performed by flowing the carrier gas through a calibrated loop filled with the mixture to analyse.

Bis (2-chloroethyl) ether was purchased from Aldrich (purity 99%), nitrogen (purity 99.995%) was obtained from Alphagaz-Air-Liquide. Bis (2-chloroethyl) sulphide (purity > 97%) and all the safety equipment required for its handling (special clothing, respiratory masks, boots and butyl gloves) were provided by 'Le Centre d'Etudes du Bouchet'. During the experiments, every item or piece of equipment, which could have been in contact with bis (2-chloroethyl) sulphide was
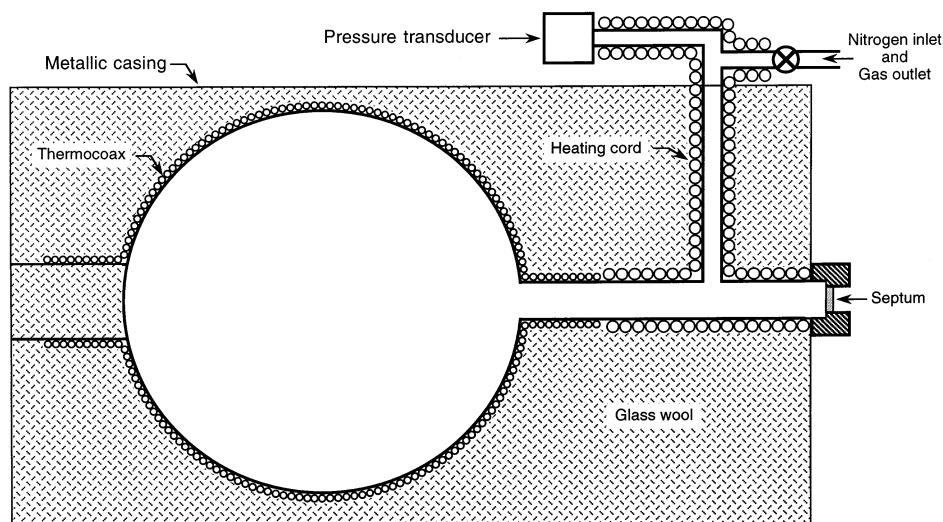

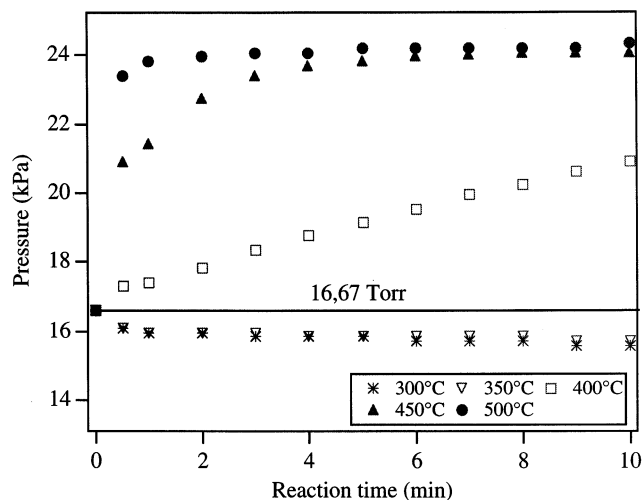Fig. 1. Scheme of the static vessel.

Fig. 2. Typical profiles of the pressure vs. time for the thermal decomposition of bis (2-chloroethyl) sulphide. Theoretical initial pressure, 16.67 kPa.

decontaminated by an alcoholic solution of sodium hydroxide. At the end of the experiments, all the remaining bis (2-chloroethyl) sulphide was destroyed in an alcoholic solution of sodium hydroxide.

3. Experimental results

3.1. The pyrolysis of bis (2-chloroethyl) sulphide

The pyrolysis of bis (2-chloroethyl) sulphide has been studied between 300 and 500°C at an theoretical initial pressure of 16.67 kPa (including 13.33 kPa of nitrogen) and a reaction time of 10 min. Fig. 2 shows typical profiles of the pressure versus time that we obtained for different temperatures. At 300–350°C, the pressure reaches instantaneously 16 kPa, a value which is slightly less than what can be derived from the volume of liquid injected (i.e. 16.67 kPa), and stays constant demonstrating that nearly all the reactant is vaporised, but that there is probably also a small part of liquid condensed on the cold zones of the reactor. A slow pressure rise at 400°C shows that the reaction is in progress. At 500°C, the pressure rises almost instantaneously and reaches a value around 24 kPa; this value corresponds to a pressure of organic compounds (excluding nitrogen) four times higher than the pressure of reactant initially vaporised.

Since it was not possible to use the internal standard method, it was difficult to obtain an accurate measurement of the conversion of the reactant. As calibration curves showed that the peak areas obtained by GC–MS for bis (2-chloroethyl) sulphide varied linearly against concentration, a comparison between chro-

matograms obtained injecting equal volumes was then possible. It showed that the area of the peak of bis (2-chloroethyl) sulphide was 100 times smaller at 450°C than at 300°C. It can then be deduced that a conversion above 99% was obtained at 450°C onwards.

Fig. 3 shows the evolution of the partial pressure of light organic products versus temperature. The main reaction products detected are ethylene and vinyl chloride. Methane, ethane and acetylene are minor products. Traces of propene have been detected.

At 450°C and for a bis (2-chloroethyl) sulphide initial pressure of 3.33 kPa, the conversion, which can be deduced by means of a carbon mass balance, from the partial pressures of the light organic products obtained, is only around 60%. Organic light compounds are then not the only main products of this reaction and some heavier compounds certainly condensed at the outlet of the reactor, since the consumption of the reactant seems complete.

The analyses by GC–MS show also the formation of carbon disulphide (CS_2), 1,2-dichloroethane, thiophene (cyclic-C_4H_4S) and methylthiophene, but since no internal standard can be introduced in the samples, it was not possible to quantify the amounts of compounds formed.

3.2. The pyrolysis of bis (2-chloroethyl) ether

The pyrolysis of bis (2-chloroethyl) ether has been studied between 300 and 500°C at an theoretical initial pressure of 16.67 kPa and a reaction time of 10 min. The profiles of pressure show some problems of vaporisation similar to those observed in the case of bis (2-chloroethyl) sulphide. The factor of pressure obtained when the reaction is complete at 500°C stands between 3.7 and 3.8.
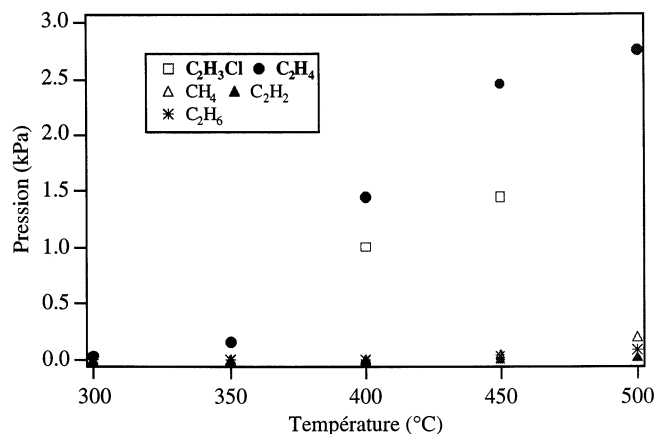

Fig. 3. Product formation during the pyrolysis of bis (2-chloroethyl) sulphide vs. temperature. Theoretical initial pressure, 16.67 kPa; reaction time, 10 min.
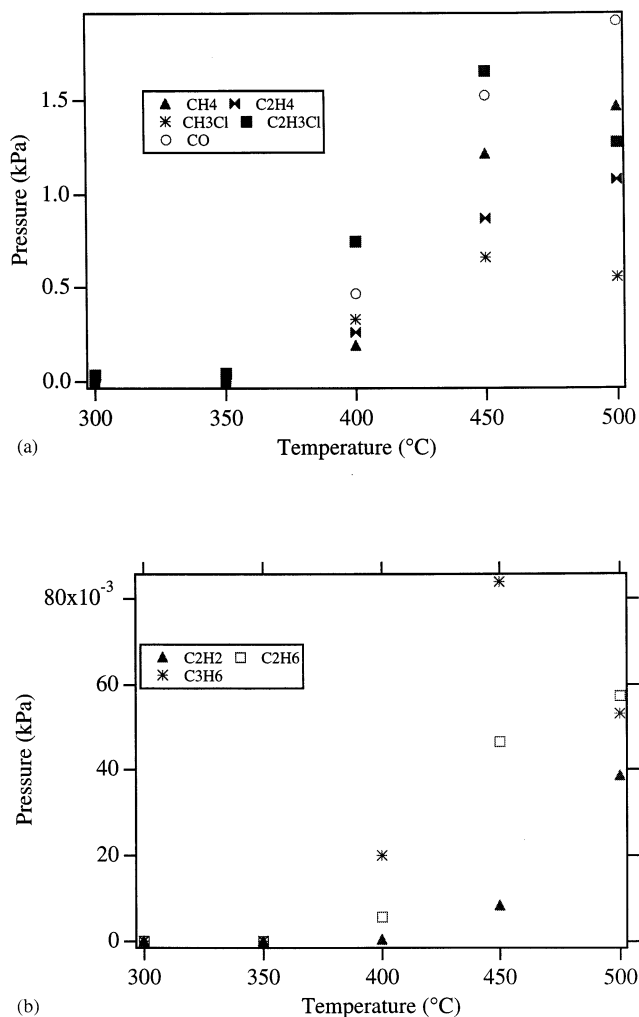
Fig. 4. Product formation during the pyrolysis of bis (2-chloroethyl) ether vs. temperature. (a) Major products, (b) minor products. Theoretical initial pressure, 16.67 kPa; reaction time, 10 min.

Here also, an accurate measurement of the conversion was difficult to obtain. A conversion around 70% at 500°C can be deduced from a comparison of the GC–MS chromatograms obtained injecting equal volumes at 350 and 500°C.

Fig. 4 shows the evolution of the partial pressure of light organic products against temperature for a reaction time of 10 min. The main reaction products detected are vinyl chloride, methyl chloride, methane, ethylene and carbon monoxide (Fig. 4a). Ethane, acetylene and propylene are minor products (Fig. 4b). At 500°C and for a bis (2-chloroethyl) ether initial pressure of 3.33 kPa, the conversion, which can be deduced by means of a carbon mass balance, from the partial

pressures of products obtained, is also around 70%. Let us point out that there is a good agreement between the two methods that we have used to estimate the conversion. The main products of reaction have then been identified. The analyses by GC–MS show no formation of heavier products (e.g. cyclic ethers).

Fig. 5 shows the evolution of the partial pressure of the major products versus reaction time at 400°C. The initial formation rate of methane and carbon monoxide is zero indicating that these are secondary[1] products while vinyl chloride, methyl chloride and ethylene seem to be primary[1] products.

Table 1 summarises the main features of the experimental conditions and results obtained in this study.

It is worth noting that the behaviour of these two compounds during their thermal decomposition presents some differences. The conversion obtained with bis (2-chloroethyl) ether is much lower than with the sulphide. Ethylene and vinyl chloride were observed in both cases. An important formation of carbon monoxide, methane and methyl chloride is also obtained when bis (2-chloroethyl) ether is used. Bis (2-chloroethyl) sulphide leads to the formation of thiophene whereas the formation of the analogous cyclic compounds (tetrahydrofurane), has not be detected in the case of bis (2-chloroethyl) ether. The kinetic analysis of the mechanisms presented below should permit to explain these differences.
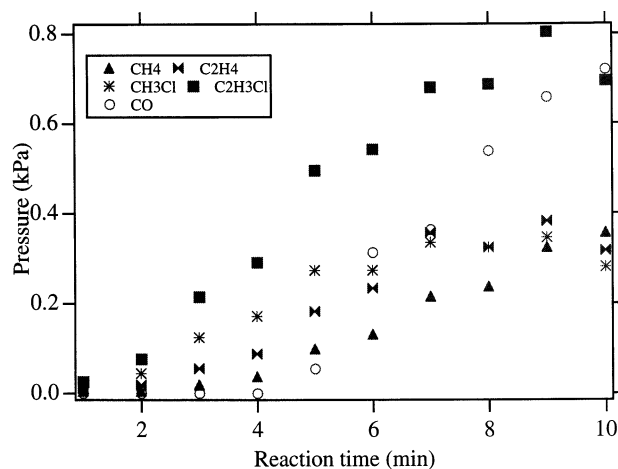

Fig. 5. Evolution of the partial pressures of the major products with reaction time during the pyrolysis of bis (2-chloroethyl) at 400°C. Theoretical initial pressure, 16.67 kPa.

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[1] The words 'primary' and 'secondary' have to be taken in their kinetic meaning.
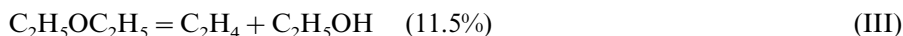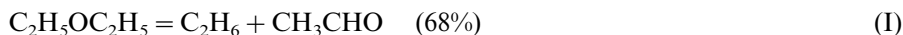
Table 1
Summary of the main experimental results[a]

Compound	Temperature (°C)	Theoretical initial pressure (kPa)	Reaction time (min)	Maximum conversion obtained (%) (at 500°C)	Products formed
Bis (2-chloroethyl) sulphide	300–500	16.67	10	≥99	**C_2H_4, C_2H_3Cl**, CH_4, C_2H_2, C_2H_6, C_3H_6, CS_2, thiophène *HCl*, *S_2*
Bis (2-chloroethyl) ether	300–500	16.67	10	≥70	**C_2H_4, C_2H_3Cl, CH_4, CO, CH_3Cl**, C_2H_2, C_2H_6, C_3H_6, *HCl*

[a] The products written in bold are the main reaction products, those written in italics have not been directly analysed.

4. Discussion

4.1. The pyrolysis of ethyl ether [3]

In a static reactor, at temperatures between 490 and 525°C and at pressures between 7 and 14 kPa, the main stoichiometric equations which have been observed accounting for the pyrolysis of ethyl ether are as follows (the relative yields are indicated in brackets)

$$C_2H_5OC_2H_5 = C_2H_6 + CH_3CHO \quad (68\%) \tag{I}$$

$$C_2H_5OC_2H_5 = H_2 + C_2H_4 + CH_3CHO \quad (12\%) \tag{II}$$

$$C_2H_5OC_2H_5 = C_2H_4 + C_2H_5OH \quad (11.5\%) \tag{III}$$

Minor products include CH_4, CH_2O, C_2H_5O, $C_2H_3OC_2H_5$ and n-C_4H_{10}.

The stoichiometric Eq. (III) is deduced from the molecular four-centre elimination Reaction 1:

$$CH_2\text{--H} \atop CH_2\text{--O--}C_2H_5 \quad \rightarrow \quad C2H4 + C2H5OH$$
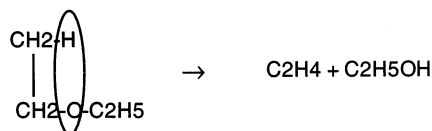
The stoichiometric Eqs. (I) and (II), which are responsible for 80% of the ether consumption are accounted for by free-radicals reactions where $C_2H_5^\bullet$ and $H^\bullet$ ($R^\bullet$) are the chain carriers. The chain propagations start by reactions of H-abstraction mainly from the carbon atom located in alpha of the oxygen atom, according to the thermodynamically favoured channel:

$$R^\bullet + CH_3CH_2\text{--O--}CH_2\text{--}CH_3 \rightarrow RH + CH_3\text{--}CH^\bullet\text{--O--}CH_2\text{--}CH_3 \tag{2}$$

The subsequent reactions are decompositions of the radical obtained.

$$CH_3\text{--}CH^\bullet\text{--O--}CH_2\text{--}CH_3 \rightarrow C_2H_5^\bullet + CH_3\text{--}CHO \tag{3}$$

$$C_2H_5^\bullet \rightarrow C_2H_4 + H^\bullet \tag{4}$$
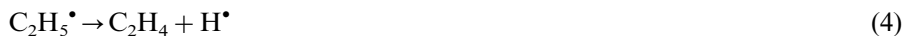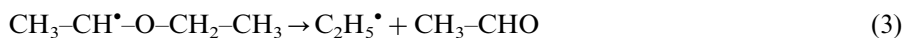
4.2. The pyrolysis of bis (2-chloroethyl) sulphide

In the case of bis (2-chloroethyl) sulphide, the molecular four-centre elimination Reaction 5 similar to Reaction 1, can also be considered
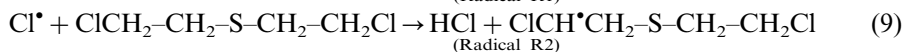
$$ClCH\text{--H} \atop CH_2\text{--S--}C_2H_4Cl \quad \rightarrow \quad C2H3Cl + CH2Cl\text{-}CH2SH$$
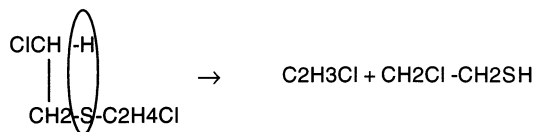
$$\tag{5}$$

The thiol $CH_2Cl–CH_2SH$ can probably decompose to give hydrochloric acid and ethylene sulphide. Previous studies have shown that ethylene sulphide can easily react to give molecular sulphur, S_2, and ethylene [10].

$$CH_2Cl–CH_2SH \rightarrow HCl + cyclo\text{-}C_2H_4S \tag{6}$$

$$2 \ cyclo\text{-}C_2H_4S \rightarrow S_2 + 2C_2H_4 \tag{7}$$

The series of Reaction 5 and Reaction 6 explains the formation of ethylene and vinyl chloride observed.

$$2ClC_2H_4–S–C_2H_4Cl = 2HCl + 2C_2H_3Cl + 2C_2H_4 + S_2 \tag{IV}$$
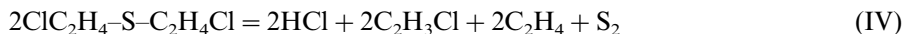
The thermal decomposition of bis (2-chloroethyl) sulphide could also occur through a free-radical mechanism, where the chain carriers would be chlorine atoms. A bis (2-chloroethyl) sulphide molecule can react by H-abstraction according to the two following steps

$$Cl^{\bullet} + ClCH_2–CH_2–S–CH_2–CH_2Cl \rightarrow HCl + \underset{\text{(Radical R1)}}{ClCH_2–CH^{\bullet}–S–CH_2–CH_2Cl} \tag{8}$$

$$Cl^{\bullet} + ClCH_2–CH_2–S–CH_2–CH_2Cl \rightarrow HCl + \underset{\text{(Radical R2)}}{ClCH^{\bullet}CH_2–S–CH_2–CH_2Cl} \tag{9}$$

Reaction 8 is thermodynamically favoured due to the presence of a sulphur atom neighbouring the radical carbon atom; but there is a possibility of isomerisation between R1 and R2 radicals.

R1 and R2 radicals can decompose by beta-scission. In the case of radical R1, as the formation of a sulphur aldehyde is difficult, the easiest reaction is the following:

$$ClCH_2–CH^{\bullet}–S–CH_2–CH_2Cl \rightarrow Cl^{\bullet} + \underset{\text{(Molecule M1)}}{CH_2{=}CH–S–CH_2–CH_2Cl} \tag{10}$$
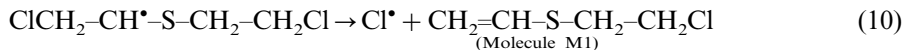
A H-abstraction on molecule M1 can lead to a cyclisation and to the formation of thiophene which has been experimentally detected. In this case stoichiometric Eq. (V) is obtained.

$$ClC_2H_4–S–C_2H_4Cl = 2HCl + H_2 + cyclo\text{-}C_4H_4S \tag{V}$$
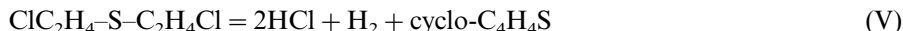
In the case of radical R2, Reaction 11 leads to the formation of vinyl chloride and ethylene sulphide, which can react according to Reaction 5 and Reaction 6 to give molecular sulphur and ethylene.

$$ClCH^{\bullet}–CH_2–S–CH_2–CH_2Cl \rightarrow ClCH{=}CH_2 + cyclo\text{-}C_2H_4S + Cl^{\bullet} \tag{11}$$
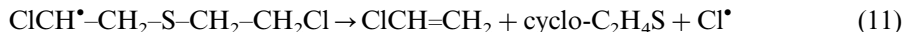
This series of reactions leads also to stoichiometric Eq. (IV) which is in line with the experimental results obtained. Eq. (IV) and Eq. (V) are in agreement with the multiplication by a factor four of the pressure of organic compounds obtained above 450°C.

4.3. The pyrolysis of bis (2-chloroethyl) ether

As in the cases of ethyl ether and bis (2-chloroethyl) sulphide, a molecular four-centre elimination (Reaction 12) can be considered

$$\text{ClCH}\text{-H} \atop \text{CH2-O-C2H4Cl} \rightarrow \text{C2H3Cl} + \text{CH2Cl-CH2OH}$$
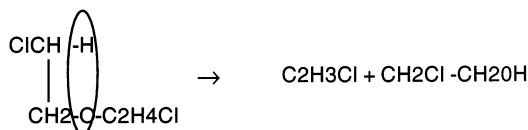
The molecule $CH_2Cl–CH_2OH$ can probably decompose to give hydrochloric acid and the oxirane which will be isomerised to acetaldehyde. It is well-known that the pyrolysis of acetaldehyde leads to methane and carbon monoxide by a free-radical mechanism [11].
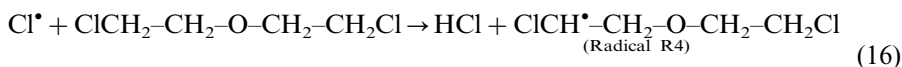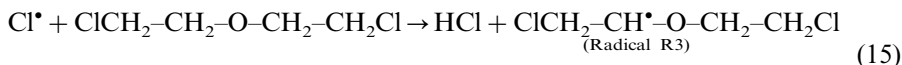
$$CH_2Cl–CH_2COH \rightarrow \rightarrow HCl + CH_3CHO \tag{13}$$

$$CH_3CHO \rightarrow \rightarrow \rightarrow CO + CH_4 \tag{14}$$

These reactions are not elementary steps.

The series of Reactions 12, 13 and 14 leads to stoechiometric Eq. (VI) which is in line with the formation of methane, carbon monoxide and vinyl chloride. In the case of yperite, the ethylene sulphide leads to the formation of ethylene and sulphur.
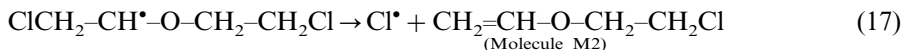
$$ClC_2H_4–O–C_2H_4Cl = HCl + C_2H_3Cl + CH_4 + CO \tag{VI}$$
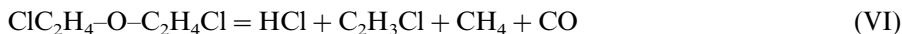
Nevertheless, as the reaction of hydrochloric acid elimination is probably slow at low temperature, the concentration of $CH_2Cl–CH_2OH$ formed can be important. But this molecule was certainly condensed at the outlet of our vessel, which explains that it was not detected in our analyses. This would also explain the lower amount of methane and carbon monoxide compared to vinyl chloride and their secondary behaviour at 400°C.

The thermal decomposition of bis (2-chloroethyl) ether can probably also take place according to a chain free-radical mechanism, where the chain carriers would be chlorine atoms. A molecule of bis (2-chloroethyl) ether can react by H-abstraction according to the two following pathways

$$Cl^{\bullet} + ClCH_2–CH_2–O–CH_2–CH_2Cl \rightarrow HCl + ClCH_2–CH^{\bullet}–O–CH_2–CH_2Cl \atop \text{(Radical R3)} \tag{15}$$

$$Cl^{\bullet} + ClCH_2–CH_2–O–CH_2–CH_2Cl \rightarrow HCl + ClCH^{\bullet}–CH_2–O–CH_2–CH_2Cl \atop \text{(Radical R4)} \tag{16}$$

Reaction 15 is thermodynamically favoured thanks to the presence of an oxygen atom neighbouring the radical carbon atom; but there is a possibility of isomerisation between the two R3 and R4 radicals. These two radicals can also decompose by beta-scissions.

There are two possibilities arising from radical R3:

$$ClCH_2–CH^{\bullet}–O–CH_2–CH_2Cl \rightarrow Cl^{\bullet} + CH_2=CH–O–CH_2–CH_2Cl \atop \text{(Molecule M2)} \tag{17}$$

$$ClCH_2–CH^{\bullet}–O–CH_2–CH_2Cl \rightarrow Cl^{\bullet} + CH_2=CH_2 + CH_2Cl–CHO \tag{18}$$

A H-abstraction on molecule M2 would lead to a cyclisation and to the

formation of tetrahydrofuranne which was not detected in experiments. Reaction 18 which is not possible in the case of bis (2-chloroethyl) sulphide gives ethylene and chloroacetaldehyde which leads probably very quickly to carbon monoxide and methyl chloride. The following stoichiometric Eq. (VII) is then obtained:

$$ClC_2H_4-O-C_2H_4Cl = HCl + C_2H_4 + CH_3Cl + CO \quad \text{(VII)}$$

Stoichiometric Eq. (VII) is in agreement with the formation of ethylene, methyl chloride and carbon monoxide. The decomposition of chloroacetaldehyde is probably very fast, this explains why methyl chloride seems to be a primary product. During the pyrolysis of bis (2-chloroethyl) sulphide, the formation of thiophene was experimentally detected, but no traces of methyl chloride were observed. In the case of sulphides, Reaction 18, which is equivalent to Reaction 10, is favoured compared to Reaction 17, of aldehyde formation, whereas it is the opposite for the oxygenated ether.

Radical R4, produces via Reaction 19 vinyl chloride which was detected in experiments and oxirane, which is isomerised to acetaldehyde which can quickly decompose to give methane and carbon monoxide

$$ClCH^\bullet-CH_2-O-CH_2-CH_2Cl \rightarrow ClCH=CH_2 + \text{cyclo-}C_2H_4O + Cl^\bullet \quad \text{(19)}$$
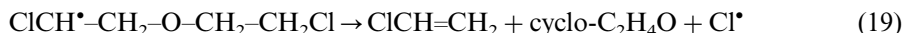
This series of reactions leads to stoichiometric Eq. (VI) which agrees with our experimental results. At high temperature, vinyl chloride can break up to produce chlorine atoms and vinyl radicals which can also become chain carriers and lead to ethylene formation.

4.4. Differences in the mechanism of thermal decomposition of bis (2-chloroethyl) sulphide and bis (2-chloroethyl) ether

For both compounds, molecular elimination and free-radical mechanism occur as well. In the free-radical mechanisms, the initiation reaction occurs by breaking of a C–S (305 kJ mol^{-1}) or C–O bond (343 kJ mol^{-1}). This reaction will be easier for bis (2-chloroethyl) sulphide, as the bond dissociation energy is lower for a C–S bond. This explains why the conversion of bis (2-chloroethyl) sulphide obtained is higher than that of bis (2-chloroethyl) ether.

Sulphur compounds do not easily lead to the formation of aldehydes, whereas this formation is easy in the case of oxygenated compounds. Carbon monoxide, methane and methyl chloride are derived from the formation of acetaldehyde and chloroacetaldehyde, which are only obtained in the case of bis (2-chloroethyl) ether. This explains why methane and methyl chloride are not important products of the thermal decomposition of bis (2-chloroethyl) sulphide. Since radical R1 (obtained from bis (2-chloroethyl) sulphide) cannot decompose to give an aldehyde, it leads to the formation of thiophene through cyclisation; in the case of radical R3 (derived from bis (2-chloroethyl) ether), cyclisation becomes negligible compared to decomposition into chloracetaldehyde and ethylene and the formation of oxygenated cyclic compounds is not detected.

5. Conclusion

The gas-phase pyrolysis of bis (2-chloroethyl) sulphide and bis (2-chloroethyl) ether has been investigated in a static reactor at temperatures between 300 and 500°C, at an initial pressure of 16.67 kPa with a dilution in nitrogen and for reaction times ranging from 1 to 10 min. The decomposition of bis (2-chloroethyl) sulphide (yperite) is close to 99% above 450°C; the major products analysed are vinyl chloride and ethylene. Thiophene, molecular sulphur and hydrochloric acid were not quantitatively analysed, but are also potential important products. The decomposition of bis (2-chloroethyl) ether leads to the formation of vinyl chloride, methyl chloride, methane, ethylene, carbon monoxide and hydrochloric acid. The differences between these two compounds have been explained by different mechanisms. This paper confirms the conclusion deduced from our study of the thermal decomposition of chloropicrin, diphosgene and phosgene [1] — an industrial process based on low pressure pyrolysis could be a feasible solution to destroy the agents included in chemical weapons.

It is worth noting that this study must be regarded as a first approach of the thermal decomposition of bis (2-chloroethyl) sulphide and bis (2-chloroethyl) ether. Due to the difficult handling of yperite, a static apparatus has been used which permitted a rather easy handling of this compound. More accurate results could have been obtained in a flow reactor, with less problems of condensation during the sampling (heavy products could certainly have been analysed). But more important amount of initial compounds would have been necessary and this would have raised the problem of the trapping and destruction of substantial amounts of unreacted yperite.

Acknowledgements

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